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WADC TECHNICAL REPORT 55-220 Pt 1
AD0093332

DEVELOPMENT OF FLUORO-SILICONE ELASTOMERS

PAUL TARRANT

PENINSULAR CHEMRESEARCH, INC.

AUGUST 1955

WRIGHT AIR DEVELOPMENT CENTER

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WADC TECHNICAL REPORT 55-220

DEVELOPMENT OF FLUORO-SILICONE ELASTOMERS

PAUL TARRANT

PENINSULAR CHEMRESEARCH, INC.

AUGUST 1955

MATERIALS LABORATORY
CONTRACT No. AF 33(600)-26593
PROJECT No. 7340
TASK No. 73404

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Carpenter Litho & Prtg. Co., Springfield, O.
300 - May 1956

FOREWORD

This report was prepared by Paul Tarrant of Peninsular ChemResearch, Inc. under USAF Contract No. AF 33(600)-26593. This contract was initiated under Project No. 7340, "Rubber, Plastic and Composite Materials", Task No. 73404, "Synthesis and Evaluation of New Polymers", formerly RDO No. 617-11, "Synthesis and Evaluation of New Polymers", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Capt. R. T. Clark, Lt. B. Weinstein, and Lt. E. C. Stump acting as project engineers.

This report covers work accomplished during the period April 5, 1954 through April 4, 1955.

The help of D. E. O'Connor, R. E. Lane, B. Silverman, F. F. Norris and G. W. Dyckes in conducting experiments and securing data is acknowledged with appreciation.

ABSTRACT

The preparation of a homopolymer from 3, 3, 3-trifluoropropylmethyldichlorosilane has been accomplished on a small scale.

Experimental conditions have been studied for the reaction of trichlorosilane and methyldichlorosilane with olefins. For hydrocarbon olefins, the best yield of addition product was obtained at 250° C without a peroxide catalyst. The use of a platinum catalyst supported on charcoal allows the use of lower reaction temperatures and shorter reaction times in these additions.

The additions of silanes to a number of fluoroölefins have been carried out. Both methyldichlorosilane and trichlorosilane have been employed as addenda and CF_2=$CFCl$, CH_2=CF_2, CHF=CF_2, CF_2=$CFCF_3$, CH_2=$CHCF_3$, CH_2=CHC_3F_7 and CH_2=$C(CF_3)CH_3$ as the fluoroölefins. The best yield by far was obtained using 3, 3, 3-trifluoropropene which gave a 72% yield of adduct, $CF_3CH_2CH_2SiCl_3$, with trichlorosilane. The physical properties of the various compounds have been determined.

Vinylsilanes have been found to react with molecules such as CCl_3Br, CF_2Br_2, CF_3I, $CF_2BrCFClBr$ and $CF_2ClCFClI$ to give compounds containing halogen atoms on an alkyl side chain. The properties of these compounds have been studied.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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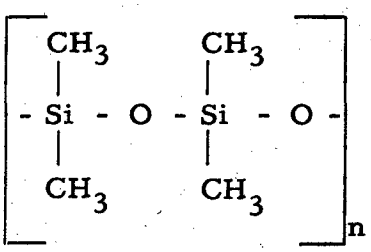
INTRODUCTION

Contract AF 33(600)-26593 has as its objective the preparation of elastomeric fluoro-silicone polymers with improved fuel and organic solvent resistance.

The preparation of a silicone rubber involves several steps which are: 1) the preparation of the monomer (such as $(CH_3)_2SiCl_2$); 2) the hydrolysis to silicone units,



3) the compounding of such materials; and finally 4) the cross linking or vulcanizing of such polymer units to the final rubber.

The research reported here is chiefly concerned with step 1, which, in this case, has to do with the development of methods of synthesis of compounds of the type $R_fSi(CH_3)X_2$ where R_f refers to an alkyl group containing fluorine and X is a hydrolyzable group such as chlorine or an alkoxy group. The preparation of compounds containing one side chain no longer than five carbon atoms has received the greatest attention since it has been found that undesirable properties are imparted when longer chains are present in elastomers. Furthermore, the presence of one methyl group on the silicon atom appears to be necessary for superior vulcanization or cross linking; therefore, the preparation of silanes containing such a group has received priority in this work.

THE PREPARATION OF SILANE MONOMERS

In general, three methods are employed for the preparation of silicon compounds containing one or more alkyl groups. These are: 1) the reaction of an alkyl halide with silicon; 2) the treatment of a silicon compound containing Si-halogen or Si-OR bonds with a Grignard reagent; and more recently 3) the addition of certain compounds containing the Si-H bond to olefins.

The first method has not been used to any considerable extent for the preparation of compounds containing fluorine in a side chain. A study has been made of the reaction of perfluoro-alkyl chlorides with silicon (10) and it has been concluded that it is impossible to prepare a trifluoromethylsilane by reacting trifluoromethyl chloride and silicon. Below 400°,* at which temperature alkyl halides react, no reaction took place with the perfluoro-alkyl chlorides. At higher temperatures, 500-1000°, an exothermic reaction took place. This reaction was not addition to the silicon to form perfluoro-alkyl chlorosilanes, but a complete transfer of halogen from carbon to silicon appeared to occur. The authors suggest the possibility of the use of the reaction for an analytical method for removing fluorine and other halogen atoms from carbon in volatile fluoro-carbons.

It is interesting to note that a recent U. S. patent (15) has been granted in which it is claimed that trifluoromethylsilicon chlorides, viz., trifluoromethyltrichlorosilane, bis-(trifluoromethyl)-dichlorosilane and tris-(trifluoromethyl)-chlorosilane, resulted from the passage of trifluoromethylchloride over copper-silicon heated for the most part between 400 and 500° C. Perfluoroethyl chloride also was reported to have given perfluoro-ethyl silicon chlorides. Other similar examples are given. In none of the examples given were the products separated or identified as such, nor were any physical, chemical or analytical properties of individual compounds given. Such a situation leaves some doubt as to whether the reaction actually proceeded as claimed in the patent.

The Grignard method for the preparation of alkylsilanes is a very useful preparative method, and, consequently, is widely used. However, the preparation of fluoro-alkylsilanes by this method seems to offer a number of difficulties. For example, no silane of the type $R_fCH_2SiX_3$ has yet been made because of the apparent inability of compounds such as CF_3CH_2Br, $CF_3CF_2CH_2Br$, etc. to form the Grignard reagent. Although compounds containing a perfluoroalkyl group separated from the silicon atom by two methylene groups have been prepared, their synthesis is rather involved as the following reactions show.

$$CF_3CF_2CF_2CO_2H + C_2H_5OH \longrightarrow CF_3CF_2CF_2CO_2C_2H_5$$

$$C_3F_7CO_2C_2H_5 + CH_3MgBr + i\text{-}C_3H_7MgBr \longrightarrow C_3F_7CHOHCH_3$$

$$C_3F_7CHOHCH_3 + P_2O_5 \longrightarrow C_3F_7CH{=}CH_2$$

*Unless otherwise indicated temperatures are given in degrees Centigrade

$$C_3F_7CH{=}CH_2 + HBr \longrightarrow C_3F_7CH_2CH_2Br$$

$$C_3F_7CH_2CH_2Br + Mg \longrightarrow C_3F_7CH_2CH_2MgBr$$

$$C_3F_7CH_2CH_2MgBr + SiCl_4 \longrightarrow (C_3F_7CH_2CH_2)_nSiCl_{4-n}$$

The reaction of the Grignard reagent with silicon tetrachloride gave tetrakis-(3, 3, 4, 4, 5, 5, 5-heptafluoropentyl)-silane (10% yield), the tris compound (47% yield), the bis compound (25% yield) and heptafluoropentyltrichlorosilane (20% yield). It can be seen that the formation of undesired, highly alkylated silanes used up a considerable portion of the fluoro Grignard reagent (16).

A somewhat later report (13) describes experimental conditions which lead to good yields of monoalkylsilanes. For example, heptafluoropentylmagnesium bromide (0.075 mole) was added to ethyl silicate (0.75 mole) to give a 71% yield of 3, 3, 4, 4, 5, 5, 5-heptafluoropentyltriethoxysilane. Even under these conditions, a 12% yield of tetrakis-(heptafluoropentyl)-silane was obtained.

It is interesting to note that elastomeric copolymers of dimethyldichlorosilane with bis-(3, 3, 4, 4, 5, 5, 5-heptafluoropentyl)-diethoxysilane, 3, 3, 4, 4, 5, 5, 5-heptafluoropentylmethyldiethoxysilane and bis-(3, 3, 3-trifluoropropyl)-dimethoxysilane have been prepared (6). Homopolymers of the fluorine-containing silanes were not formed. The copolymers had improved resistance to the swelling action of fuels and retained other desirable physical properties. These elastomers had greater stability in diester oils at elevated temperatures than methyl silicone rubber prepared in the same way or the commercially available silicone rubber. The fluorine-containing elastomers retained over 50% of their tensile strength after 24 hours in diester oil at 400° F while the nonfluorine-containing materials dissolved at 350° F.

The synthesis of silanes containing a perfluoroalkyl group appears to be a difficult operation by the Grignard method. In the first place, the use of a Grignard reagent from a perfluoroalkyl halide and magnesium requires such vigorously controlled experimental conditions that the yields of desired products from Grignard reactions are often low.

It has been reported (16) that perfluoropropylmagnesium iodide reacted with silicon tetrachloride and ethyl silicate to give tarry materials, with no indication of the formation of stable fluorine-containing silanes. On the basis of the separation of trimethylsilane from a

reaction of trimethylchlorosilane and the perfluoropropyl Grignard reagent in tetrahydrofuran as the solvent, the investigators who conducted the study have concluded that the failure to form the fluorinated silane resulted because of the attack of the Grignard reagent on the solvent.

The addition of silanes containing the Si-H bond to olefins has been the subject of several investigations. For instance trichlorosilane was added to octene-1 in the presence of acetyl peroxide to give octyltrichlorosilane in 99% yield (22). Trichlorosilane and octene-1 gave a 24% yield of adduct when irradiated by a weak source of ultraviolet radiation. In an extension of this research (19) trichlorosilane was added to the following olefins in the yields indicated: 2-methyl-1-heptene, 70%; 2-methyl-2-butene, 24.6%; 2,3-dimethyl-2-butene, 59.3%; 2,4,4-trimethyl-1-pentene, 9.1%; 2,4,4-trimethyl-2-pentene, 9.3%; 1,1-dineopentylethylene, 1.6% and allyl chloride, 20.4%.

Analogous results were reported by a second group (5) who reported addition products (yields in parenthesis) from 1-pentene (73%), cyclohexene (64%), vinyltrichlorosilane (19%), allyltrichlorosilane (83%), isobutylene (10%), and acetylene (3%); conversions were of the order of 30%. It was also found that methyldichlorosilane added to 1-pentene (37%) and 2-pentene (71%).

A communication appeared in 1947 describing the thermal addition of silanes to various olefins (4). For example, n-propylmethyldichlorosilane was prepared in 72% yield by heating propylene and methyldichlorosilane overnight at 300°. A wide variety of compounds were prepared by this procedure which offers the advantage of a reaction mixture uncontaminated by the decomposition products from the peroxides used as catalyst.

The patent literature on the production of silanes by the addition of a silane to olefins is fairly extensive. However, because of the diverse claims and experimental procedures described, it is difficult to get a general idea of the scope or mechanism of the reaction. For instance, patents have been issued which describe as catalyst peroxides (3,11), aluminum chloride (8), platinum on charcoal (27), and in some cases, reaction has been shown to proceed without any of these substances (20).

The first experimental work carried out on this contract consisted of efforts directed toward the establishment of satisfactory

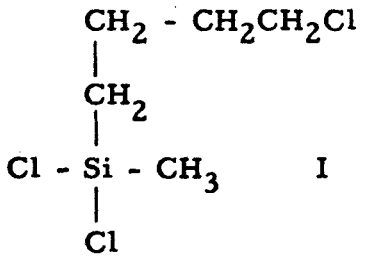
reaction conditions for the additions of trichlorosilane and methyldichlorosilane to hydrocarbon olefins. The olefins selected for the study were propene, 2-methylpropene and butene-2 because they have been found to take part readily in free-radical catalyzed reactions (24). However, it was found that neither silane reacted with propene to give an addition product when heated to 85° for four hours in the presence of benzoyl peroxide in a stainless steel reaction vessel.

It was thought that the use of a peroxide decomposing at a higher temperature might be more effective in causing the reaction to take place and di-t-butyl peroxide, 2-methylpropene and methyldichlorosilane were heated to 140° for two hours. A very small amount of product boiling in the range expected for the addition product was isolated when the reaction mixture was distilled. Although the literature indicates that trichlorosilane gives higher yields of adducts than methyldichlorosilane, the addition of trichlorosilane to 2-methylpropene at 150° for four hours with di-t-butyl peroxide gave very little adduct, $(CH_3)_2CHCH_2SiCl_3$, which is a known compound.

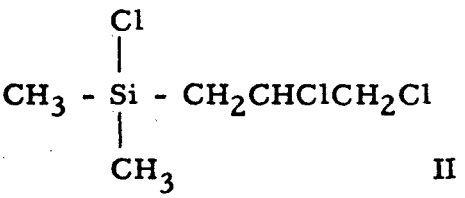
Chlorotrifluoroethylene and methyldichlorosilane, when heated with catalytic amounts of benzoyl peroxide, gave a small amount (2-3 g) of a product whose properties, b.p. 61-70° at 20 mm, n_D^{24} 1.4472, d_4^{24} 1.5145, MR_D calcd. for $C_3H_4Cl_3F_3Si$ 39.10, MR_D found 40.86, indicate it to be the addition product.

The situation with respect to reaction conditions became more complex when it was found that some reaction took place when olefins and a silane containing no silicon-to-hydrogen bonds, viz., dimethyldichlorosilane,were heated in the presence of benzoyl peroxide. It would appear that some addition product was obtained from 2-methylpropene and dimethyldichlorosilane since a small amount (5 g) of material boiling at 119-131° was separated. The physical constants agreed fairly well with those expected for the product but the hydrolyzable chlorine value was 28.9% whereas that required for $(CH_3)_2SiClCH_2CCl(CH_3)_2$ is 19.3% and for $Cl_2Si(CH_3)CH_2CH_2CH(CH_3)_2$ is 38.6%. The former adduct would result if a Si-Cl bond is broken and addition then takes place, the latter could result through the removal by peroxide of a hydrogen atom from the methyl group of dimethyldichlorosilane. It would appear from the analytical data that the latter course had been followed.

A small amount of product was also obtained when allyl chloride, dimethyldichlorosilane and benzoyl peroxide were heated. This material boiled at about 110° and its molar refraction was not too greatly different from that calculated for the addition product I or II. Again some hydrolyzable chlorine was present but the value was only 25% of that expected for the adduct.



I



II

It should be pointed out that considerable difficulty is encountered in the processing of small amounts of silanes containing more than one hydrolyzable chlorine atom per molecule. The reaction products must be distilled without the usual processing such as washing which removes acidic by-products. Furthermore, the silanes hydrolyze rapidly, often in the distillation apparatus, and freeze the ground glass connections. And, finally, the addition products are obtained by distillation only after the unreacted starting materials are removed, and, consequently, unless large amounts of adducts are formed in the reaction, little material boiling over a narrow temperature range can be separated.

In view of the results described above, it was decided that more drastic conditions were needed, and a study was made of the reaction of butene-2 with trichlorosilane at elevated temperatures. The first run was carried out at 200° in a stainless steel reaction vessel using di-t-butyl peroxide (4 g) as catalyst with 0.79 mole of silane and 0.63 mole of the olefin. An arbitrary time of four hours was chosen for the series of reactions as no pressure gage was available so that the drop in pressure as reaction progressed could be noted. In this experiment a yield of crude adduct, $CH_3CH_2CH(CH_3)SiCl_3$, of 11.5% was formed. A second experiment was carried out at 250° under the same conditions as described above and a 32.3% yield of the adduct was obtained. In a third experiment conducted at 250° C in the absence of peroxide, a 63% yield of product was obtained. It thus appeared that optimum conditions for the addition of trichlorosilane to butene-2 involve elevated temperatures (above 200°) without a peroxide catalyst. It seems strange that the presence of a peroxide would actually lower the yield of the addition product below that obtained in its absence.

Methyldichlorosilane and butene-2 were then heated at 200° without catalyst but very little addition occurred under these conditions.

It was felt that enough information about reaction conditions was available so that the reaction between fluoro-olefins and silanes at elevated temperatures could be studied. The first experiment was carried out at 200° without catalyst using 1.3 moles of trichlorosilane and 0.73 mole of chlorotrifluoroethylene. One fraction of 10 g was obtained, b.p. 120-137°, which apparently contained chiefly the desired adduct since the analytical values were reasonably close to the theoretical values when the wide range over which the sample was collected is taken into consideration.

In an effort to determine the influence of higher reaction temperatures on the yields and also to obtain more samples for better purification, a run was begun at 250°. A 1.4 liter stainless steel reaction vessel was employed in which 2.2 moles of trichlorosilane and 1.6 moles of chlorotrifluoroethylene were heated. Apparently some exothermic reaction began at about 250° as the temperature continued to rise beyond this point to about 300° even though heating was discontinued. A rather violent explosion resulted at this point and the fittings were blown from the head of the reaction vessel. The rupture disc used on the vessel was broken thus indicating that no gradual increase in pressure inside the vessel was responsible for its failure.

Previous investigators of peroxide catalyzed reactions of perhaloalkyl compounds to olefins and fluoroölefins have shown that the best yields of addition products are obtained from hydrocarbon olefins or olefins containing a methylene group. For example, dibromodifluoromethane reacted with propylene to form $CF_2BrCH_2CHBrCH_3$ and with $CH_2{=}CFCH_3$ to give $CF_2BrCH_2CFBrCH_3$ but it did not form a simple addition product with chlorotrifluoroethylene (24, 25). Similar results have been described using $CF_2BrCFClBr$ and $CF_2ClCFClI$ (23, 26). It is interesting to note that $CF_2{=}CHCH_3$ does not form $CF_2ClCFClCF_2CHICH_3$ with $CF_2ClCFClI$ but instead gives the branched chain compound thus indicating the unreactivity of the difluoromethylene group toward participation in telomerization reactions. Another indication of the reluctance of compounds containing the $CF_2{=}C-$ group to accept other substance by free radical attack is given by the fact that compounds such as $CF_2{=}CFCH{=}CF_2$ and $CF_2{=}C(CH_3)CF{=}CF_2$ are very difficult to polymerize (12).

It therefore seemed appropriate to study silane additions to fluoro-olefins which contained a methylene group. A small scale

experiment was carried out using 3, 3, 3-trifluoropropene, $CF_3CH{=}CH_2$, and trichlorosilane and a small amount of material (12 g) was obtained when the reaction was carried out at 250° for 20 hours. A larger scale run gave very good results. In it, trifluoropropene (100 g) and trichlorosilane (380 g) were heated to 275° for four hours and, by distillation, a 72% yield of 3, 3, 3-trifluoropropyltrichlorosilane was obtained. The physical properties were determined on a center fraction of this material and are given in Table II.

Trichlorosilane also added readily to 2-fluoropropene to form the adduct $CH_3CHFCH_2SiCl_3$. This compound is similar to other β-haloalkylsilanes in losing the β-halogen when treated with base. However, hydrolysis in distilled water gave a neutral equivalent of 65.8 which corresponds well with the value required if only the chlorine atoms are removed.

A recent U. S. Patent (27) describes the use of platinum on charcoal as catalyst for the addition of silanes to olefins. One of the examples describes the addition of trichlorosilane to vinylidene fluoride. This experiment was repeated and a very small amount (2-3 g) of adduct, $CHF_2CH_2SiCl_3$, b.p. 104-106°, obtained. This yield (1.5%) is somewhat lower than that obtained in the patent but it is interesting to note that the compound does not lose hydrogen fluoride when treated with the base used during neutral equivalent determination.

Trifluoroethylene, trichlorosilane and platinum catalyst were heated to 150° for four hours without forming any addition products.

Attempts to prepare 3, 3, 3-trifluoropropylmethyldichlorosilane by the reaction of 3, 3, 3-trifluoropropyltrichlorosilane and methylmagnesium bromide were unsuccessful. A product was obtained which contained a mixture of starting material and methylated product which could not be separated by distillation. Fortunately, methyldichlorosilane reacted readily with 3, 3, 3-trifluoropropene to give the desired product, the properties of which are given in Table I. The yield of adduct was about 50%.

The additions of methyldichlorosilane to 2-trifluoromethylpropene and 3, 3, 4, 4, 5, 5, 5-heptafluoropentene were also attempted. Very small amounts of products believed to be the addition products were formed; however, enough material was obtained in each case to determine physical constants and to analyze for chlorine and satisfactory results were obtained.

The results claimed (27) as a result of the catalytic effect of platinum on the addition of silanes to olefins warranted an investigation of its effectiveness in promoting reactions with fluoroolefins. It is disclosed that a small amount of platinum supported on charcoal greatly reduced the time and temperature required for reaction. For example, at 160° acetylene reacted with trichlorosilane for one hour in the presence of about 0.6 g of charcoal containing 0.05% platinum gave vinyltrichlorosilane (60%) and bis-(trichlorosilyl)-ethane (15%). Even triethoxysilane was found to take part in addition reactions and a 50% yield of vinyltriethoxysilane was obtained from acetylene. Under essentially the conditions listed above, allyl chloride, which has been reported to give 20% of 3-chloropropyltrichlorosilane when refluxed 27 hours with acetyl peroxide, formed the adduct in 51% yield with platinum catalyst at 150-160° for about fifty minutes. Trichlorosilane also reacted with trichloroethylene and vinylidene fluoride under these conditions to give $CCl_2{=}CHSiCl_3$ (35%) and $CHF_2CH_2SiCl_3$ (10%), respectively.

It seemed that the use of platinum catalyst might be of considerable value in reactions with chlorotrifluoroethylene. It should be noted that the use of chlorotrifluoroethylene as a starting material in the synthesis of elastomeric materials is particularly desirable for several reasons. It can be obtained commercially without difficulty. Its use in plastics and elastomers to give materials with superior properties is well known: the chemical resistance of polychlorotrifluoroethylene is second only to that of Teflon, and rubber-like materials containing chlorotrifluoroethylene (such as Kel-F Elastomer manufactured by the M. W. Kellogg Co.) are resistant to oxidizing agents such as fuming nitric acid and do not swell appreciably in organic fuels. Chlorotrifluoroethylene has also been found to take part in free radical reactions better than the perfluoroölefins with the possible exception of tetrafluoroethylene.

However, before carrying out additions to chlorotrifluoroethylene, it seemed advisable to examine some of the experiments described for use with the platinum catalyst. It was found that allyl chloride gave 32% adduct and vinylidene fluoride 2%. Although these values are less than those described in the patent, it seems that platinum is of some use in facilitating the addition of silanes containing the Si-H bond.

An experiment was then carried out with chlorotrifluoroethylene and methyldichlorosilane at 200° for 3-3/4 hours with a small amount

of the platinum catalyst from which 70 g of material boiling at 109-129° was separated. Over a narrow range of 126-129°, 58 g of adduct was obtained. The yield of crude product was 20%; however, analysis for total chlorine and hydrolyzable chlorine was slightly greater than the theoretical value for the adduct. In order to obtain more material for more efficient purification, a second run was carried out as above and a 24% yield of crude addition product separated. A third run was made without incident and the product set aside for processing with that from a fourth experiment which was to be carried out under the same conditions. However, a violent explosion occurred and the reaction vessel, an American Instrument Company rocking autoclave rated at about 10,000 psi, was so expanded in the heating jacket that it could not be removed.

The product from the several runs above was distilled through an efficient fractionating column to give about 25 g of a fraction, b.p. 128.5 - 130°, for which constants were determined. These constants show that the material is the one-to-one addition product, $C_2HClF_3Si(CH_3)Cl_2$.

THE ADDITION OF PERHALOALKANES TO VINYLSILANES

It is of some interest to note that vinylsilanes take part in many of the reactions in which other vinyl compounds participate. For example, vinyltrichlorosilane reacts with hydrogen chloride in the presence of aluminum chloride to form chloroethyltrichlorosilane and vinyltrimethylsilane adds hydrogen bromide in the presence of peroxides to give bromoethyltrimethylsilane (21). The latter reaction is different from that found with most vinyl compounds as the direction of addition of the acid is reversed.

It seemed that compounds containing fluorine on a side chain could be produced by reacting certain vinylsilanes with fluorohaloalkanes and a study was initiated to test this idea. Both vinyltrichloro- and vinyltrimethylsilane were employed and, in most cases, satisfactory amounts of addition products were obtained. The properties of these compounds are listed in Table III. Of the two silanes, the trichloro compound was found to be less reactive for it did not react with dibromodifluoromethane or iodotrifluoromethane. However, reaction occurred with CCl_3Br and $CF_2ClCFClI$.

It is interesting to note that the proof of structure of the addition products was not difficult as compounds of structures I or II would result.

$CCl_3CH_2CHBrSiCl_3$ (I) $\qquad$ $CH_2BrCH(CCl_3)SiCl_3$ (II)

The compound represented by I does not have halogen in the β-position and, consequently, the hydrolyzable halogen is due entirely to that resulting from hydrolysis of the Si-Cl bond. Experimentally it was found that hydrolyzable chlorine values indicated that compounds of the type represented by I were obtained. It is interesting that addition to vinyltrimethylsilane also gave compounds in which the perhalo-alkyl group was attached to the carbon atom beta to the silicon atom.

Some information has been obtained about the chemical properties of these addition products of vinylsilanes and perhaloalkanes. For instance, it appears that the fluorination of $CCl_3CH_2CHBrSiCl_3$ takes place readily to give compounds which contain Si-F bonds. Very little replacement of halogen on the alkyl group occurred. This course of the reaction is to be expected since the replacement of chlorine attached to silicon occurs readily; undoubtedly, if an adequate sized sample of $CCl_3CH_2CHBrSiF_3$ was treated with a fluorinating agent, some replacement of alkyl bound halogen would result.

The adduct from $CF_2BrCFClBr$ and vinyltrimethylsilane was treated with potassium hydroxide and an olefin whose properties agree with those expected for $CF_2BrCFClCH{=}CHSi(CH_3)_3$ resulted.

THE PREPARATION OF INTERMEDIATES

Considerable effort was expended in preparing intermediates for use in the various reactions which were carried out during the course of this research.

3, 3, 3-Trifluoropropene was prepared by a series of reactions as shown:

$$CF_2Br_2 + CH_2{=}CH_2 \longrightarrow CF_2BrCH_2CH_2Br$$

$$CF_2BrCH_2CH_2Br + HF \longrightarrow CF_3CH_2CH_2Br + HBr$$

$$CF_3CH_2CH_2Br + KOH \longrightarrow CF_3CH{=}CH_2 + KBr + H_2O$$

Although the yields in each of the first two steps were somewhat low, satisfactory amounts of the products were made by carrying out repeated runs.

The preparations of the other olefins were carried out by methods described in the literature.

THE POLYMERIZATION OF 3, 3, 3-TRIFLUOROPROPYLMETHYLDICHLOROSILANE

The addition product from 3, 3, 3-trifluoropropene and methyldichlorosilane was hydrolyzed by the procedure used at Wright Air Development Center to give copolymers from heptafluoropentylsilanes (6). This method involved the treatment of 30 g of $CF_3CH_2CH_2Si(CH_3)Cl_2$ with 10% hydrochloric acid for several hours to give a low molecular weight polymer. Treatment of this material with sodium hydroxide at temperatures up to 200° gave a viscous liquid. A small sample of material obtained under the same conditions except that the final treatment was carried out at a lower temperature was sent to the Center for evaluation.

TABLE I. THE ADDITION OF METHYLDICHLOROSILANE TO FLUORO-OLEFINS

Olefin	Product	B. P., °C	Pressure mm	t °C	n_D^t	d_4^t	ANALYSIS Hydrolyzable Cl Calcd.	Found
$CF_2=CFCl$	$CHFClCF_2Si(CH_3)Cl_2$	128.5-130	760	21.5	1.4036		30.7	30.8
$CF_3CH=CH_2$	$CF_3CH_2CH_2Si(CH_3)Cl_2$	122	760	20	1.3946	1.2611	33.6	33.5
$CH_3-C(CF_3)=CH_2$	$CH_3-CH(CF_3)CH_2Si(CH_3)Cl_2$	144	760	24	1.3971		31.6	31.4
$C_3F_7CH=CH_2$	$C_3F_7CH_2CH_2Si(CH_3)Cl_2$	76	77	24	1.3700		22.8	23.0

TABLE II. THE ADDITION OF TRICHLOROSILANE TO FLUORO-OLEFINS

Olefin	Product	B. P. °C	Pressure mm Hg.	t °C	n_D^t	d_4^t	ANALYSIS Hydrolyzable Cl Calcd	Found
$CH_2{=}CF_2$	$CHF_2CH_2SiCl_3$	104-106	760				53.2	49.6
$CH_2{=}CFCH_3$	$CH_3CHFCH_2SiCl_3$	123-124	760	21.5	1.4348	1.1924	54.5	54.0
$CF_3CH{=}CH_2$	$CF_3CH_2CH_2SiCl_3$	114	760	28	1.3845	1.3951	46.1	46.3

TABLE III. THE ADDITION PRODUCTS FROM VINYLSILANES AND PERHALOALKANES

Compound	B. P., °C	Pressure mm Hg.	t °C	n_D^t	d_4^t	Calcd	Found
$CCl_3CH_2CHBrSiCl_3$	140-143	40	23	1.5247	1.8196	29.7	28.6[a]
$CF_2ClCFClCH_2CHISiCl_3$	120-140	15				24.3	23.8[a]
$CF_3CH_2CHISi(CH_3)_3$	67-70	17	23	1.4481	1.5057	42.9	43.4[b]
$CF_2BrCH_2CHBrSi(CH_3)_3$	84	17	22.5	1.4638	1.5521^{16}	51.7	51.9[c]
$CCl_3CH_2CHBrSi(CH_3)_3$	96-98	5-7	22	1.5045	1.4150^{34}	74.6	75.3[d]
$CF_2ClCFClCH_2CHISi(CH_3)_3$	70	1	25	1.4779	1.6074^{16}	126.3	
$CF_2BrCFClCH_2CHBrSi(CH_3)_3$	85	5	25	1.4647	1.6022	125.5	122.7[d]

a. Hydrolyzable Chlorine

b. Iodine

c. Bromine

d. Silver Equivalent

EXPERIMENTAL

I. The Addition of Silanes to Olefins

A. Hydrocarbon Olefins and Silanes

1. The Addition of Methyldichlorosilane to 2-Butene

$$CH_3CH{=}CHCH_3 + CH_3SiHCl_2 \longrightarrow CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HSi(CH_3)Cl_2$$

2-Butene (26 g, 0.46 mole) and methyldichlorosilane (90 g, 0.782 mole) were heated at 200° and rocked for four hours in the absence of catalyst. The reaction product was distilled to give unreacted methyldichlorosilane (66 g) and about 3.6 g of material, b.p. 120-126°, which was assumed to be the adduct.

2. The Addition of Trichlorosilane to 2-Butene

$$CH_3CH{=}CHCH_3 + HSiCl_3 \longrightarrow CH_3\text{-}CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HSiCl_3$$

In an effort to find reaction conditions which lead to satisfactory yields of addition products, a study was made of the reaction of trichlorosilane with 2-butene. These reactions were carried out in a stainless steel vessel of 300 ml capacity for a period of four hours. The conditions and results are summarized in Table IV below.

TABLE IV

The Reaction of Trichlorosilane and 2-Butene

Run	2-Butene		Trichlorosilane		D-t-butyl Peroxide	Temp. °C	YIELD	
	g.	Mole	(g)	(Mole)	(g)		Wt., g.	%
1	35	0.625	106	0.786	4	200	13.7	11.5
2	42	0.75	106	0.786	4	250	46.3	32.2
3	43.4	0.775	106	0.786	0	250	93.5	63.2

The product was distilled through an 18" column packed with glass helices and the fraction collected at 135-154° used for comparison although most of the material in this fraction distilled at 144°.

It is evident that preferred conditions are 250° and four hours without a catalyst.

B. The Addition of Trichlorosilane to Fluoroölefins

1. The Addition of Trichlorosilane to Vinylidene Fluoride

$$CH_2{=}CF_2 + HSiCl_3 \longrightarrow CHF_2CH_2SiCl_3$$

The 1.4 liter reaction vessel was loaded with trichlorosilane (203 g, 1.5 moles) and 0.5 g of platinum catalyst (Baker and Company, Inc., 5% platinum on charcoal, lot no. 2060) and the vessel sealed. Vinylidene fluoride was added from a cylinder until the pressure in the vessel was 200 psi. The vessel was then heated to 200° for 4 hours. The product was distilled through a 12" column packed with glass helices and 3 g of $CHF_2CH_2SiCl_3$, b.p. 104-106°, obtained. The yield in this reaction was 1.5% based on trichlorosilane under these conditions. Anal. Calcd. for $C_2H_3Cl_3F_2Si$: hydrolyzable Cl, 53.2. Found: hydrolyzable Cl, 49.6%.

The neutral equivalent was found to be 64.5 while the neutral equivalent of $CHF_2CH_2SiCl_3$ is 66.4 if only the silicon-chlorine bond is broken.

2. Reaction of Trichlorosilane and Trifluoroethylene

The reaction vessel was charged with trichlorosilane (136 g, 1 mole), trifluoroethylene (64 g, 0.8 moles) and catalyst (0.5 g) and heated to 150° for 4 hours. The contents of the vessel were distilled and, after removal of 107 g of unreacted silane (30-40°), 2 g of material boiling at 66-78° were obtained.

3. The Addition of Trichlorosilane to Chlorotrifluoroethylene

a. At 150° C

Chlorotrifluoroethylene (155 g, 1.33 moles), trichlorosilane (271 g, 2.0 moles) and commercial platinum catalyst on charcoal

(0.5 g) were added to the 1.4 liter reaction vessel and heated to 150° for 4 hours. The unreacted starting material was removed by distillation through a 27" column and a 5 g fraction, b.p. 95-125°, was obtained.

Anal. Calcd. for $C_2HCl_4F_3Si$: hydrolyzable Cl, 42.3. Found: hydrolyzable Cl, 58.5%.

In a second run, chlorotrifluoroethylene (106 g, 0.9 moles), trichlorosilane (191 g, 1.4 moles) and catalyst (0.5 g) were heated and agitated in a pressure vessel for 30 hours at 150°. The product from the reaction was distilled but, after removal of the unreacted starting material, not enough high boiling product remained for further distillation.

b. At 200° C

Chlorotrifluoroethylene (196 g, 1.68 moles), trichlorosilane (271 g, 2.0 moles) and platinum catalyst (0.5 g) were heated and agitated at 200° for three hours. Ten grams of product was obtained boiling at 123-131°, when distilled through a 27" column. However, the hydrolyzable chlorine content was only 28.1% while the theoretical for the addition product is 42.3%.

4. The Addition of Trichlorosilane to 2-Fluoropropene

$$CH_3CF{=}CH_2 + HSiCl_3 \longrightarrow CH_3CHFCH_2SiCl_3$$

A 1.4 liter reaction vessel was cooled in Dry-Ice and trichlorosilane (532 g, 4.08 moles) and 2-fluoropropene (118 g, 2.0 moles) added. The vessel was rocked and heated to 240° where a pressure of 1050 psi developed. At the end of fourteen hours the pressure had dropped to 750 psi and heating was discontinued. After venting the residual pressure while the vessel was cooled in ice, the product was removed and distilled through a 27" column. The addition product was collected at 120-130° C and amounted to 28 g. A center fraction had the properties as listed: b.p. 123-124°, $n_D^{21.5}$ 1.4348, $d_4^{21.5}$ 1.1924. Anal. Calcd. for $C_4H_9Cl_3FSi$: hydrolyzable Cl, 54.5; neutral. eq. 48.9. Found: hydrolyzable Cl (Volhard), 54.0; neutral. eq. 51.5. Hydrolysis in distilled water gave a neutral equivalent of 65.8 indicating that the fluorine was not removed in acid media.

The lower neutral equivalent determined by adding an excess of the base, viz., 51.5, could only be obtained by hydrolysis of the fluorine as well as the chlorine atoms and demonstrates that one fluorine atom in a position beta to a silicon atom is not resistant to hydrolysis.

5. The Addition of Trichlorosilane to 3, 3, 3-Trifluoropropene

$$CF_3CH{=}CH_2 + HSiCl_3 \longrightarrow CF_3CH_2CH_2SiCl_3$$

A small scale run was carried out at 250° for twenty hours with 3, 3, 3-trifluoropropene (29 g) and trichlorosilane (80 g). A 12 g fraction of material was obtained boiling over the range 90-120°. Some material was lost in loading the autoclave and no yield was calculated. However, a larger scale reaction at 250° for sixteen hours and 275° for four hours using 100 g of olefin and 380 g of the silane gave 172 g (72% yield) of $CF_3CH_2CH_2SiCl_3$. The physical properties on a center fraction of this material are b.p. 114°, n_D^{28} 1.3845, d_4^{28} 1.3951, MR_D Calcd. 38.52. MR_D fd. 38.85. Anal. Calcd. for $C_3H_4Cl_3F_3Si$: hydrolyzable Cl, 46.1. Found: hydrolyzable Cl, 46.3.

C. The Addition of Methyldichlorosilane to Fluoroölefins

1. The Reaction of Methyldichlorosilane with Chlorotrifluoroethylene

$$CF_2{=}CFCl + CH_3SiHCl_2 \longrightarrow H(C_2F_3Cl)Si(CH_3)Cl_2$$

The reaction of the silane (235 g, 2.04 moles) with chlorotrifluoroethylene (175 g, 1.5 moles) was carried out in a stainless steel vessel heated to 200° for three and three-quarter hours. A commercial 5% platinum on charcoal catalyst was used in small amount (0.7 g). The reaction mixture was distilled through a column and, after removal of the excess methyldichlorosilane, the following fractions were separated:

Fraction No.	Temperature, °C	Weight, g.
1	60-66.3	61
2	66-109	14
3	109-126	12
4	126-128	30
5	128.6-129.0	28
Residue		62

Fractions 3, 4 and 5 were considered to contain chiefly the desired adduct, $C_2HF_3ClSi(CH_3)Cl_2$. Analysis of the material in fraction 5, which had a n_D^{22} 1.4167 and d_4^{20} 1.4411, for total chlorine, hydrolyzable chlorine by Volhard and acid-base titration gave values of 47.5, 32.4 and 32.7%, respectively. The corresponding theoretical values are 46.1, 30.7 and 30.7.

A second addition was carried out as described above with about the same ratio of reactants, chlorotrifluoroethylene (201 g, 1.72 moles) and methyldichlorosilane (265 g, 2.30 moles). About twice as much low boiling (60°) material was obtained in addition to the following fractions.

Fraction No.	Temperature, °C	Weight, g
1	60-66.5	59
2	66.5-109	33
3	109-126	20
4	126-138	37
Residue		90

A third run was carried out using about the same conditions as noted above without incident. However, a fourth run with CF_2=CFCl (211.5 g, 1.81 moles), methyldichlorosilane (269 g, 2.34 moles) and platinum catalyst (0.5 g) detonated.

The product from the three successful runs was combined and redistilled through a 27" column packed with glass helices. The material boiling in the range 110-145° (70 g) was redistilled, through a micro-column, and product (25 g) distilling at 128.5-130° obtained. The physical constants for this material are $n_D^{21.5}$ 1.4036, d_4^{20} 1.4036. Anal. Calcd. for $C_3H_4Cl_2F_3Si$: hydrolyzable Cl, 30.7. Found: hydrolyzable Cl (by Volhard), 30.8.

A series of experiments was carried out using lower temperatures and a peroxide catalyst as described below. The autoclave was charged with methyldichlorosilane (115 g, 1 mole), chlorotrifluoroethylene (30 g, 0.26 mole) and benzoyl peroxide (2 g), and heated to 80° for four hours without agitation. The vessel was then cooled in Dry-Ice, opened and the product poured into a flask attached to traps cooled in Dry-Ice. About 36 g of low boiling material was collected in the traps indicating that little reaction had occurred. Distillation of the remainder was carried out and 88 g of methyldichlorosilane, b.p. 33-42°, was recovered. About 10 g of residue was left.

A second run was carried out with one mole of olefin and one-half mole of silane at 100° for four hours. Again a small amount of residue was obtained after removal of unreacted starting material. The residue was distilled at 20 mm where a fraction (2-3 g) was obtained with the following properties: b.p. 61-70 at 20 mm, n_D^{24} 1.4472, d_4^{24} 1.5145. It should be noted that these properties are considerably different from those found for the material obtained by the reaction of CH_3SiHCl_2 and CF_2=CFCl without catalyst.

2. The Addition of Methyldichlorosilane to 3, 3, 3-Trifluoropropene

$$CF_3CH{=}CH_2 + CH_3SiHCl_2 \longrightarrow CF_3CH_2CH_2Si(CH_3)Cl_2$$

A stainless steel autoclave was cooled in Dry-Ice and loaded with methyldichlorosilane (345 g, 3.0 moles), 3, 3, 3-trifluoropropene (105 g, 1.1 moles) and 5% platinum on charcoal (0.5 g). The clave was closed, rocked and heated at 200° for four hours. The contents were removed and distilled through a 27" column packed with glass helices. The following data were obtained:

Fraction No.	Temperature, °C	Weight, g.
1	22-62	149
2	62-111	69
3	111-122	32
4	122	91

The material in fraction 4 was the desired $CF_3CH_2CH_2Si(CH_3)Cl_2$, b.p. 122°, n_D^{20} 1.3946, d_4^{20} 1.2611. Anal. Calcd. for $C_4H_7Cl_2F_3Si$: hydrolyzable Cl, 33.6. Found: hydrolyzable Cl, 33.5.

3. The Addition of Methyldichlorosilane to 2-Trifluoromethylpropene

$$CH_3\text{-}\overset{\displaystyle CF_3}{\overset{|}{C}} = CH_2 + CH_3SiHCl_2 \longrightarrow CH_3\text{-}\overset{\displaystyle CF_3}{\overset{|}{C}}HCH_2SiCl_2 \quad (CH_3)$$

The reaction of methyldichlorosilane (51 g, 0.45 moles) and 2-trifluoromethylpropene (49 g, 0.45 moles) was carried out in a stainless steel reaction vessel heated to 250° C for six hours. The vessel was opened with very little gas pressure and the reaction mixture distilled through a column; the following fractions were separated:

Fraction No.	Temperature, °C	Weight, g
1	40-42	5.0
2	42-44	19.0
3	44-81	8.0
4	81-130	2.0
5	130-138	2.0
6	138-150	4.7
Trap		40
Residue		5

It was thought that fraction 5 and 6 contained the desired adduct,

$$CH_3\overset{\displaystyle CF_3}{\overset{|}{C}}HCH_2Si(CH_3)Cl_2$$

Analysis of fraction 5, which had a n_D^{23} 1.3951, for hydrolyzable chlorine by Volhard titration gave a value of 31.4. The theoretical value for hydrolyzable chlorine is 31.6.

4. The Addition of Methyldichlorosilane to 3, 3, 4, 4, 5, 5, 5-Heptafluoropentene

$$CF_3CF_2CF_2CH{=}CH_2 + CH_3SiHCl_2 \longrightarrow CF_3CF_2CF_2CH_2CH_2Si(CH_3)Cl_2$$

The addition of methyldichlorosilane (47 g, 0.41 mole) to 3, 3, 4, 4, 5, 5, 5-heptafluoropentene (80 g, 0.41 mole) was carried out in a stainless steel reaction vessel heated to 250° C for six hours. The reaction mixture was distilled through a column and the following high boiling fractions were separated at a pressure of 77 mm.

Fraction No.	Temperature, °C	Weight, g
1	42-74	6.2
2	74-78	2.5
3	78-84	3.0

It was thought that fractions 2 and 3 contained the desired adduct, $CF_3CF_2CF_2CH_2CHSi(CH_3)Cl_2$. The refractive index of fraction 2 was 1.3700 at 24°. Volhard titration for hydrolyzable chlorine gave a value of 23.0. The theoretical value for hydrolyzable chlorine is 22.8.

II. Peroxide Catalyzed Additions to Vinylsilanes

A. To Vinyltrichlorosilane

1. The Addition of Bromotrichloromethane to Vinyltrichlorosilane

$$CCl_3Br + CH_2{=}CHSiCl_3 \xrightarrow{Bz_2O_2} CCl_3CH_2CHBrSiCl_3$$

A solution of benzoyl peroxide (5 g) in 198 g of bromotrichloromethane was added dropwise to a refluxing mixture of vinyltrichlorosilane (161 g, 1 mole) and bromotrichloromethane (198 g, 1 mole). Reflux was maintained for five hours after the addition was completed. The excess bromotrichloromethane was removed at 40-50° at 70-80 mm and three fractions were obtained at 105-150° at about 40 mm, although most of the material distilled at 140-150°. The yield of addition product was 55%.

A second run made under essentially the same conditions produced 320 g (60%) of $CCl_3CH_2CHBrSiCl_3$, b.p. 130-150 at 40 mm. A third larger scale run gave 950 g (66%) of crude adduct.

A center fraction from the distillation of one of these runs gave material having the following properties: b.p. 140-143° at 40 mm, n_D^{23} 1.5247, d_4^{23} 1.8196. Anal. Calcd. for $C_2H_3BrCl_6Si$: hydrolyzable Cl, 29.7. Found: hydrolyzable Cl, 28.6.

It should be noted that the formation of $CH_2BrCH(CCl_3)SiCl_3$ in the reaction between CCl_3Br and $CH_2{=}CHSiCl_3$ would lead to hydrolyzable chlorine values considerably higher than the values actually obtained because of the ease of hydrolysis of halogen atoms in the beta-position. Consequently, the adduct must have the structure $CCl_3CH_2CHBrSiCl_3$.

2. The Addition of 1,2-Dichloro-1-iodo-1,2,2-trifluoroethane to Vinyltrichlorosilane

$$CF_2ClCFClI + CH_2{=}CHSiCl_3 \xrightarrow{Bz_2O_2} CF_2ClCFClCH_2CHISiCl_3$$

A mixture of benzoyl peroxide (6 g) and vinyltrichlorosilane (162 g, 1 mole) was added dropwise to a flask containing 1,2-dichloro-1-iodo-1,2,2-trifluoroethane, which was heated to about 75°. About one-half hour after the addition of the silane, a vigorous reaction took place and some material was expelled from the reaction flask.

Severe foaming was encountered in attempts to distill the reaction mixture through a column. However, distillation directly from the flask gave the adduct (55 g), b.p. 120-140° at 15 mm. Anal. Calcd. for $C_4H_3Cl_5F_3I$: hydrolyzable Cl, 24.3. Found: hydrolyzable Cl, 23.8.

B. To Vinyltrimethylsilane

1. The Addition of Iodotrifluoromethane to Vinyltrimethylsilane

$$CF_3I + CH_2{=}CHSi(CH_3)_3 \longrightarrow CF_3CH_2CHISi(CH_3)_3$$

A stainless steel reaction vessel was cooled in Dry-Ice and loaded with trifluoromethyl iodide (125 g, 0.64 mole), vinyltrimethylsilane (64 g, 0.64 mole) and t-butyl peroxide (6 g). The vessel was rocked and heated for four hours at 125°. The contents were fractionated and material boiling above 164° was collected. This product was redistilled from a micro-claisen flask to give the adduct (14 g), $CF_3CH_2CHISi(CH_3)_3$, b.p. 67-70° at 17 mm, n_D^{23} 1.4481, d_4^{23} 1.5057. Anal. Calcd. for $C_6H_{12}F_3ISi$:I, 42.9. Found: I, 43.4.

2. The Addition of Dibromodifluoromethane to Vinyltrimethylsilane

$$CF_2Br_2 + CH_2{=}CHSi(CH_3)_3 \longrightarrow CF_2BrCH_2CHBrSi(CH_3)_3$$

Vinyltrimethylsilane (25 g, 0.25 mole), dibromodifluoromethane (105 g, 0.5 mole) and benzoyl peroxide (2 g) were added to a 300 ml stainless steel reaction vessel, which was then sealed, rocked and heated at 100° for four hours. The vessel was cooled in ice, opened, and the products removed. The reaction mixture was distilled through a micro-claisen column to give 65 g of unreacted starting materials and a fraction boiling at 70° with decomposition. Vacuum was applied to the system and 57 g of material boiling at 67-100° at 70 mm was obtained with most of the product distilling at 70°.

The fraction was redistilled through a 4" column packed with Berl saddles and topped with a variable-rate take-off head. Approximately 41 g of $CF_2BrCH_2CHBrSi(CH_3)_3$ were obtained at 80-84° under 16-17 mm vacuum. A fraction of 16 g collected at 84.0 at 17 mm had these properties: n_D^{22} 1.4638, d_4^{16} 1.5521. Anal. Calcd. for $C_6H_{12}Br_2F_2Si$: Br, 51.7. Found: Br, 51.9.

Undoubtedly yields greater than the 51% obtained in this experiment are possible since handling losses were somewhat large.

3. The Addition of Bromotrichloromethane to Vinyltrimethylsilane

$$CCl_3Br + CH_2{=}CHSi(CH_3)_3 \longrightarrow CCl_3CH_2CHBrSi(CH_3)_3$$

A mixture of vinyltrimethylsilane (50 g, 0.5 mole) and bromotrichloromethane (100 g, 0.5 mole) was placed in a flask and refluxed while a solution of benzoyl peroxide (6 g) in bromotrichloromethane (98 g, 0.5 mole) was added dropwise. Refluxing was continued for 20 hours. The one-to-one addition product, $CCl_3CH_2CHBrSi(CH_3)_3$, was obtained in a yield of 75%. Its properties are: b.p. 96-98° at 5-7 mm, n_D^{22} 1.5045, d_4^{34} 1.4150. Anal. Calcd. for $C_6H_{12}BrCl_3Si$: Ag. eq., 74.6. Found: Ag. eq., 75.3; hydrolyzable halogen, 0.00.

4. The Addition of 1,2-Dichloro-1-iodo-1,2,2-trifluoroethane to Vinyltrimethylsilane

$$CF_2ClCFClI + CH_2{=}CHSi(CH_3)_3 \longrightarrow CF_2ClCFClCH_2CHISi(CH_3)_3$$

The perhaloethane (137 g, 0.37 mole), silane (25 g, 0.25 mole) and benzoyl peroxide (2 g) were placed in a flask equipped with a reflux condenser and heated to 110° for fifteen minutes. The flask was then cooled and an additional amount (2 g) of peroxide added and the mixture heated to 105° for twelve hours.

Distillation of the product through a 4" column gave the one-to-one addition product, 67 g, 56% yield, $CF_2ClCFClCH_2CHISi(CH_3)_3$, b.p. 68-78° at 1 mm, a center fraction of which had a b.p. 70° at 1 mm, n_D^{25} 1.4779, d_4^{16} 1.6074.

5. The Addition of 1,2-Dibromo-1-chloro-1,2,2-trifluoroethane to Vinyltrimethylsilane

$$CF_2BrCFClBr + CH_2{=}CHSi(CH_3)_3 \longrightarrow CF_2BrCFClCH_2CHBrSi(CH_3)_3$$

A mixture of $CF_2BrCFClBr$ (153 g, 0.55 mole), vinyltrimethylsilane (30 g, 0.3 mole) and benzoyl peroxide was heated at 90° for eight hours. The reaction mixture was processed as described above and $CF_2BrCFClCH_2CHBrSi(CH_3)_3$ (98 g, 80% yield) obtained at 88° at 3.5 mm.

A second, larger scale run was made and 700 g of the adduct were obtained. A center fraction obtained during the fractionation had the properties: b.p. 85° at 5 mm, n_D^{25} 1.4646, d_4^{25} 1.6022. Anal. Calcd. for $C_7H_{12}Br_2ClF_3Si$: Ag. eq., 125.5. Found: Ag. eq. 122.7.

C. Some Reactions of the Addition Products

1. The Reaction of 3-Chloro-1, 4-dibromo-3, 4, 4-trifluorobutyltrimethylsilane with Potassium Hydroxide

$$CF_2BrCFClCH_2CHBrSi(CH_3)_3 + KOH \longrightarrow CF_2BrCFClCH{=}CHSi(CH_3)_3$$

A solution of potassium hydroxide (50 g) in methanol (100 ml) was added dropwise to $CF_2BrCFClCH_2CHBrSi(CH_3)_3$ (100 g) in a 500 ml flask equipped with a stirrer, reflux condenser and addition funnel. A heavy white precipitate was formed immediately and considerable heat was evolved. After addition of the base, the mixture was heated to 50-60° for six hours. The reaction products were allowed to stand overnight before the potassium bromide was filtered. The $CF_2BrCFClCH{=}CHSi(CH_3)_3$ (31 g) was collected at 60-65° at 8 mm when fractionated through an 18" column packed with 1/8" glass helices. The yield was 39%. A constant boiling fraction had properties as follow: b. p. 65° at 8 mm, n_D^{24} 1.4324, d_4^{23} 1.3495.

Anal. Calcd. for $C_7H_{11}BrClF_3Si$: Ag. eq. 147.6. Found: Ag. eq. 147.7.

2. The Fluorination of 1-Bromo-3, 3, 3-trichloropropyltrichlorosilane

a. With Potassium Fluoride

$$CCl_3CH_2CHBrSiCl_3 + KF/H_2SO_4 \longrightarrow CCl_3CH_2CHBrSiClF_2 + CCl_3CH_2CHBrSiF_3$$

Potassium fluoride (305 g, 5.3 moles) was placed in a flask fitted with a stirrer, addition funnel and condenser. Sulfuric acid (96%, 650 ml) was added slowly and the flask cooled in ice water. After completion of the dropwise addition of the silane (270 g, 0.75 mole), the flask was heated to 100° for one-half hour. The liquid was decanted and the solid mass extracted with two portions of ether. The liquid was dried and distilled through a 30" column packed with helices. After removal of the ether, the chief fraction (101 g) was collected at 60-70° at 15 mm.

Analytical data indicate that a mixture of products was obtained since a hydrolyzable chlorine value of 5% was found, whereas the theoretical value for $CCl_3CH_2CHBrSiF_2Cl$ is 10.8%. Total halogen determined by Parr bomb indicated a silver equivalent value of 79.3 which is intermediate between that for $CCl_3CH_2CHBrSiF_3$ (77.6) and $CCl_3CH_2CHFSiF_3$ (83.0).

b. With Antimony Trifluoride

Antimony trifluoride (213 g, 1.2 moles) was ground and placed in a glass flask equipped with stirrer, reflux condenser and dropping funnel. The adduct (180 g, 0.5 moles) from vinyltrichlorosilane and bromotrichloromethane was added slowly. Reaction began immediately and considerably heat was evolved. The reaction flask was cooled in ice-water. After the addition of the adduct, the mixture was allowed to warm to room temperature for one hour then heated to about 75°. The product was fractionated through a Claisen head and 95 g of material boiling at 110-130° and largely flat at 125-128° was obtained. Chlorine analysis showed the material to contain 5.6% chlorine.

A second run under essentially the same conditions produced 171 g of 110-130° material.

It should be noted that the purification of this material is difficult as it cannot be washed to free it of halogen acids which usually result in fluorination reactions with antimony trifluoride.

The fluorinated product (80 g) was treated with freshly distilled quinoline at 0° and a black viscous reaction product resulted from which no material could be separated by distillation.

The fluorinated adduct (45 g) and hydrogen fluoride (50 g) were heated in a 300 ml autoclave at 100° for seven hours. Some hydrogen chloride was present when the clave was opened. The mixture was poured onto sodium fluoride to absorb the excess hydrogen fluoride but no liquid layer was left. Possibly some replacement of chlorine by fluorine in the side chain occurred, but because of the difficulties involved in separation of the products from the excess hydrogen fluoride, it was impossible to obtain the organic product.

3. Attempted Preparation of $CCl_3CH_2CHBrSi(CH_3)_3$ by the Reaction of $CCl_3CH_2CHBrSiCl_3$ with Methylmagnesium Bromide

Methylmagnesium bromide was prepared in the usual manner from magnesium (36 g, 1.5 moles), methyl bromide (143 g, 1.5 moles) and ether (ca 200 ml) and added to $CCl_3CH_2CHBrSiCl_3$ (180 g). Stirring was continued for one hour after the addition. Dilute sulfuric acid was added and the ether layer separated and dried. The product was beginning to distill at 135° at 53 mm when the contents of the distillation flask suddenly solidified.

III. The Preparation of Intermediates

A. 1,3-Dibromo-1,1-difluoropropane (24)

In a typical run, dibromodifluoromethane (950 g) and benzoyl peroxide were added to a 1.4 liter stainless steel reaction vessel cooled in ice-water. A valve and pressure gage was attached and ethylene added to a pressure of 500 psi. The reaction vessel was rocked while ethylene was added as the pressure dropped. When the pressure remained at 500 psi, heat was applied and a temperature of 85-90° C maintained for four hours.

The reaction vessel was then cooled and the contents removed. Generally, the products from three experiments were combined and distilled through a 27" column packed with glass helices. The desired $CF_2BrCH_2CH_2Br$ was removed at 55-60° at 70 mm and averaged about 590 g per batch from three runs.

Some twenty experiments were carried out as described above.

B. 3-Bromo-1,1,1-trifluoropropane (25)

$$CF_2BrCH_2CH_2Br + HF \longrightarrow CF_3CH_2CH_2Br + HBr$$

A stainless steel reaction vessel was cooled in ice-water and 1,3-dibromo-1,1-difluoropropane (792 g, 3.3 moles) and hydrogen fluoride (281 g, 14 moles) added. The vessel was sealed and heated and rocked at 150° for fifteen hours. The vessel was cooled, the gas vented and the product poured onto ice and neutralized with sodium carbonate solution. The organic layer was separated, steam distilled and dried. Fractionation through a 30" column gave $CF_3CH_2CH_2Br$ (117 g), b.p. 61-65°, and recovered starting material 350 g. The yield was about 20%.

Two runs were carried out using a total amount of 927 g of $CF_2BrCH_2CH_2Br$, 385 g of hydrogen fluoride and 24 ml of antimony pentachloride as catalyst under otherwise the same conditions. The desired $CF_3CH_2CH_2Br$(286 g) was obtained in a yield of 41.5%.

Several runs were made to accumulate quantities of this bromo compound.

C. 3,3,3-Trifluoropropene (25)

$$CF_3CH_2CH_2Br + KOH \longrightarrow CF_3CH{=}CH_2 + KBr + H_2O$$

Potassium hydroxide (254 g) was dissolved in ethanol (700 ml) and the solution added dropwise to 3-bromo-1, 1, 1-trifluoropropane (267 g) with stirring. The mixture was gently refluxed for four hours after the addition was completed while the gaseous product was collected in traps immersed in Dry-Ice. The product was distilled through a vacuum jacketed column and the propene (100.5 g, 67% yield) collected at -24 to -20° C.

Additional runs were made under approximately the same conditions to supply the olefin as needed.

D. The Preparation of 2-Fluoropropene (1)

1. $CH_2ClCHClCH_2Cl + KOH \longrightarrow CH_2{=}CClCH_2Cl + KCl + H_2O$

2. $CH_2{=}CClCH_2Cl + HF \longrightarrow CH_3CFClCH_2Cl$

3. $CH_3CFClCH_2Cl + Mg \longrightarrow CH_3CF{=}CH_2 + MgCl_2$

The first step in the synthesis was carried out by heating 1, 2, 3-trichloropropane (5 kg) with a 10% sodium hydroxide solution and distilling the olefin as it formed. The product from two such runs were combined and distilled to give 2, 3-dichloropropene-1 (3.3 kg), b.p. 92-95° C.

The fluorination reaction was carried out by charging a cooled reaction vessel with dichloropropene (1100 g) and hydrogen fluoride (210 g) and allowing the reactants to rock at 30° for fifteen hours. The vessel was opened, ice added cautiously and the water layer decanted. The organic layer was neutralized with sodium carbonate solution and steam distilled. The product from two experiments was combined and treated with bromine until the color persisted. The desired 1, 2-dichloro-2-fluoropropane (950 g), b.p. 87-90° was obtained by distillation through a 30" column packed with glass helices. Almost 500 ml of high boiling material, presumably $CH_2ClCBrClCH_2Br$, were obtained indicating that the fluorination step had not been carried to completion.

Two dehalogenation experiments were carried out on $CH_3CFClCH_2Cl$ by stirring a mixture of magnesium, diethyl ether and the dichloride at reflux temperature for three days. From such runs, employing a total of 393 g of 1, 2-dichloro-2-fluoropropane, only 58 g of 2-fluoropropene were obtained. An experiment with

dichloride (117 g), dibutyl ether (600 ml) and magnesium 24 g) carried out at the reflux temperature, which was considerably higher than with diethyl ether, failed to give any olefin and the starting materials were recovered.

However, it was found that satisfactory yields of 2-fluoropropene could be obtained by employing a considerable excess of magnesium. For example, a 71% yield of olefin was obtained in one day by stirring magnesium (60 g, 2.5 moles), 1,2-dichloro-2-fluoropropane (196 g, 1.5 moles) and diethyl ether (500 ml), once the reaction had been initiated by a small amount of ethyl iodide. It was necessary to add the fluorine compound dropwise to prevent excessive refluxing of the ether. A second such experiment using essentially the same conditions gave a 72% yield of the desired olefin.

E. The Synthesis of 2-Trifluoromethylpropene

1. $CF_3CO_2H + C_2H_5OH \longrightarrow CF_3CO_2C_2H_5$

2. $CF_3CO_2C_2H_5 + 2CH_3MgBr \longrightarrow CH_3\overset{\displaystyle CF_3}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}CH_3$

3. $CH_3\overset{\displaystyle CF_3}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}CH_3 + P_2O_5 \longrightarrow CH_2{=}\overset{\displaystyle CF_3}{\overset{|}{C}}CH_3$

The first step in the synthesis was carried out by heating trifluoroacetic acid (685 g) and ethanol (310 g) in a 3 liter distilling flask and distilling off the ester as it formed. The ethyl trifluoroacetate was dried by distillation from P_2O_5, giving 779 g of ester boiling at 62-64° C for a 92% yield.

The preparation of 2-trifluoromethylpropanol-2 was accomplished by placing magnesium (110 g) and n-butyl ether (1500 ml) in a 3 neck, 3 liter flask equipped with a gas addition tube, stirrer and reflux condenser. Methyl bromide was bubbled into the solution until all of the magnesium had been converted to the Grignard reagent, CH_3MgBr. Ethyl trifluoroacetate (250 g) mixed with 500 ml n-butyl ether was then added, and finally the solution was hydrolyzed with 1 liter of 10% H_2SO_4. The ether layer was separated from the

water and dried over $CaSO_4$. The solution was then distilled giving 125 g of an azeotrope containing 75% 2-trifluoromethylpropanol-2 and 25% ethanol boiling at 80-84° C.

The conversion of 2-trifluoromethylpropanol-2 to trifluoromethylpropene was carried out in an apparatus consisting of a 3 neck, 3 liter flask fitted with an addition funnel, thermometer, electric stirrer, heating mantle, and an 8" packed column topped with a variable rate distilling head leading to a bubble counter and two Dry-Ice-acetone cold traps connected in series. Phosphorus pentoxide (125 g) was placed in the flask and 2-trifluoromethylpropanol-2 (125 g) was added slowly via the addition funnel. Heating and stirring were continued until no more bubbles were registered in the bubble counter, the 2-trifluoromethylpropene being collected in the cold traps. Fractionation of the products collected in the cold traps yielded 49 g of 2-trifluoromethylpropene boiling at 7 - 9° C.

F. Perfluoropropene (7)

1. $C_3F_7CO_2H + NaOH \longrightarrow C_3F_7CO_2Na$

2. $C_3F_7CO_2Na \longrightarrow CF_3CF{=}CF_2 + NaF + CO_2$

Perfluorobutyric acid (364 g) was neutralized with sodium hydroxide solution and the water evaporated. Alcohol (200 ml) was added and the salt dissolved. This mixture was then evaporated to dryness and the salt dried in a vacuum desiccator over phosphoric anhydride. The powdered material was heated to 175° in a flask connected to traps immersed in Dry-Ice. Perfluoropropene (145 g), b.p. -20 to -15°, was obtained corresponding to a yield of 56%.

G. 3,3,4,4,5,5,5-Heptafluoropentene

1. $C_3F_7CO_2H + CH_3OH \longrightarrow C_3F_7CO_2CH_3$

2. $C_3F_7CO_2CH_3 + CH_3MgBr + (CH_3)_2CHMgBr \longrightarrow C_3F_7CHOHCH_3$

3. $C_3F_7CHOHCH_3 + P_2O_5 \longrightarrow CF_3CF_2CF_2CH{=}CH_2$

The first two steps were carried out according to the method of McBee (18). Perfluorobutyric acid (428 g) heated for twenty-four hours with methanol (128 g) and sulfuric acid (96, 100 ml) gave a 93.4% yield of methyl perfluorobutyrate, b.p. 79.5 - 81°.

The carbinol was prepared from magnesium (85 g), ether (700 ml), methyl bromide (147 g) and isopropyl bromide (239 g) and methyl perfluorobutyrate (390 g). After standing overnight, the reaction mixture was decomposed with 2 liters of 10% sulfuric acid. Distillation gave 260 g of $CF_3CF_2CF_2CHOHCH_3$, b.p. 97-103°, which corresponds to a yield of 71% based on ester.

An attempt was made to dehydrate the carbinol (260 g) with phosphoric anhydride (142 g) suspended in benzene. However, no reaction had occurred after two days. The benzene was removed by distillation and the viscous residue was heated to 230° and the product removed as formed by using a distilling column attached to the flask. Refractionation of the product gave material (80 g, 32% yield) boiling at 32-33°, the infrared spectrum of which indicated the presence of the carbon-carbon double bond, C-H and C-F bonds.

H. The Synthesis of Trifluoroethylene

1. $CF_2=CFCl + HBr \longrightarrow CF_2BrCHFCl$

2. $CF_2BrCHFCl + Zn \longrightarrow CF_2=CHF$

The first step was carried out by the method of Park (14), using a 44" length of black iron pipe of 1-1/2" diameter which was wound with nichrome heating wire. A batch of catalyst consisting of 75% by volume of charcoal and 25% of calcium sulfate was added to the pipe and activated by heating to 200-250° for two hours at 5 to 20 mm pressure.

A stream of chlorotrifluoroethylene (0.033 mole/min) was mixed with hydrogen bromide (0.032 mole/min) and introduced into the reactor heated to about 300°. After about 1-1/2 hours the rate was increased to 0.067 mole/min for 1-1/2 hours. The product was collected in receivers cooled in ice water while unreacted chlorotrifluoroethylene was condensed in traps immersed in Dry-Ice. The crude product from this run amounted to 890 g. The product from several such runs was combined and distilled to give $CF_2BrCHFCl$ (1250 g), b.p. 53-60°.

Other experimental conditions were studied in an attempt to improve the process. Glass tubing was used instead of the iron pipe but the life of the catalyst was seriously shortened by the development of intense hot spots in the catalytic mass. Charcoal without calcium sulfate was decidedly inferior as a catalyst. It was found that activation of the catalyst by heating under vacuum was necessary.

A somewhat smaller (30" long, 1" diameter) pipe was used successfully for the addition reaction under a variety of flow rates for the olefin and hydrogen bromide, which does not appear to be a critical factor.

The dehalogenation reaction was carried out by the usual method. Yields of trifluoroethylene were about 80%.

I. The Preparation of 3-Bromo-3, 3-difluoropropene (25)

The adduct from dibromodifluoromethane and ethylene (357 g, 1.5 moles) was placed in a 3 neck flask with addition funnel, fractionating column head connected to cold traps, and stirrer. The flask was heated to about 80° and potassium hydroxide (200 g) in ethanol (600 ml) added slowly. The product was removed at 65-80° and washed with water. Distillation gave 71 g of material, b.p. 38-39°, which is undoubtedly the olefin, and a considerable amount (95 g) of higher boiling material and residue.

J. The Addition of $CF_2BrCFClBr$ to Ethylene

Two experiments were carried out essentially as described for the preparation of $CF_2BrCH_2CH_2Br$ and 361 g of $CF_2BrCFClCH_2CH_2Br$ was separated at 70-75° at 25 mm. In each run, 1125 g of $CF_2BrCFClBr$, 15 g of benzoyl peroxide and ethylene charged twice to a pressure of 400 psi in the 1.4 liter reaction vessel were reacted.

K. The Preparation of 4-Bromo-3-chloro-3, 4, 4-trifluorobutene (25)

The adduct from above (J) (361 g, 1.2 moles) was heated while alcoholic potassium hydroxide was added dropwise. The reaction product was removed by distillation as it formed. The olefin was washed several times with water and dried over calcium chloride. The olefin, $CF_2BrCFClCH{=}CH_2$ (109 g, 41%) was obtained at 97-99° C.

L. The Preparation of 1, 1, 2-Trifluorobutadiene (21)

Zinc dust (39 g, 0.6 mole) and ethanol (150 ml) were placed in a flask fitted with stirrer, addition funnel and reflux condenser connected to traps immersed in Dry-Ice. The mixture was heated to reflux and $CF_2BrCFClCH{=}CH_2$ (109 g, 0.5 mole) was added dropwise over a period of about two hours. The product was collected in the traps and distilled into a second receiver, then transferred by evaporation to a cylinder. The diene (47 g) was not distilled through a column as it polymerizes quite rapidly.

M. The Preparation of 1, 2-Dichloro-1-iodo-1, 2, 2-trifluoroethane (2)

1, 1, 2-Trichloro-1, 2, 2-trifluoroethane (400 g) and iodine chloride (589 g) were added to a suction flask and chlorotrifluoroethylene (350 g) passed through the mixture until all had dissolved. The product, $CF_2ClCFClI$, boiling at 101-102°, was obtained in 77% yield.

N. Vinyltrimethylsilane

$$CH_2{=}CHSiCl_3 + 3CH_3MgBr \longrightarrow CH_2{=}CHSi(CH_3)_3 + 3MgClBr$$

Several runs were carried out on the preparation of the silane. Using diethyl ether as the solvent, yields of 22 and 38% were obtained. The improved yield was obtained when fractions intermediate between ether (b.p. 35°) and vinyltrimethylsilane (b.p. 55°) were refractionated.

The best yield (47%) was obtained using dibutyl ether as the solvent. The Grignard reagent was obtained from methyl bromide (1413 g, 14.9 moles) and magnesium (420 g, 17.3 moles) and dibutyl ether (5 liters). Ethyl iodide (10 ml) was used to catalyze the reaction but it was necessary to employ a temperature of 40-50° to initiate reaction. Vinyltrichlorosilane (775 g, 4.8 moles) was added dropwise. The mixture became viscous and dibutyl ether (1 liter) was added and stirring continued for 4 hours. The mixture was allowed to stand overnight and hydrolyzed and distilled. Vinyltrimethylsilane (228 g, 47%) was obtained at 54-56°.

O. The Preparation of Methylchloromethyldichlorosilane

$$(CH_3)_2SiCl_2 + Cl_2 \longrightarrow CH_2ClSi(CH_3)Cl_2 + HCl$$

Dimethyldichlorosilane (529 g, 4.1 moles) was placed in a flask equipped with a stirrer, condenser and gas inlet tube. The flask was illuminated by a 100-watt lamp placed directly above and about 6 inches from it while chlorine (271 g, 2.1 moles) was bubbled into the silane. The flask was cooled by ice water during the addition of the chlorine. Distillation of the chlorinated product from two runs through a 27" column gave the amounts listed below.

	RUN 1	RUN 2
Dimethyldichlorosilane	336 g	229 g
Methylchloromethyldichlorosilane (b.p. 118-124°, flat at 121-122°)	115 g (47%)	41 g (30%)

P. The Synthesis of Dimethylchloromethylchlorosilane

$$(CH_3)_3SiCl + Cl_2 \longrightarrow CH_2ClSi(CH_3)_2\,Cl + HCl$$

Trimethylchlorosilane (108 g, 1 mole) was placed in a 3 neck flask equipped with a stirrer, condenser connected to a cold trap and gas inlet tube. Chlorine (34.5 g) was passed through the silane until all had reacted. Light from a 100 watt lamp was used to catalyze the chlorination. The desired product, b.p. 113-117°, was obtained by distillation. The yield of dimethylchloromethylchlorosilane was 47%.

Two other runs were made as described above but on a somewhat larger scale. In the larger run, 1.4 kg of trimethylchlorosilane was chlorinated to give 490 g of $CH_2ClSi(CH_3)_2Cl$ with a recovery of 597 g of $(CH_3)_3SiCl$.

IV. Miscellaneous Reactions

A. The Attempted Synthesis of 3,3,3-Trifluoropropylmethyldichlorosilane by the Grignard Reaction

$$CH_3MgBr + CF_3CH_2CH_2SiCl_3 \longrightarrow CF_3CH_2CH_2\overset{CH_3}{\overset{|}{Si}}Cl_2$$

Methylmagnesium bromide was prepared from magnesium (8 g, 0.33 mole) and methyl bromide and added dropwise to 3,3,3-trifluoropropyltrichlorosilane (159 g, 0.687 mole) over a period of one hour. The reaction mixture was distilled through a 12" column packed with glass helices and fitted with a variable-rate takeoff head. After removal of the low boiling material, two fractions were collected; the first of these boiled at 113-118° where 70.2 g was collected and the second at 118-119° where 44.8 g was obtained.

Anal. Calcd. for $C_4H_7Cl_2F_3Si$: hydrolyzable Cl, 33.2. Calcd. for $C_3H_4Cl_3F_3Si$: hydrolyzable Cl, 46.2. Found: hydrolyzable Cl, 41.4%.

It can be seen that the analytical data indicated a mixture of the desired product and unreacted starting material was obtained.

B. The Preparation of $(CH_3)_3SiCH_2CF=CCl_2$

Reactions:

1. $(CH_3)_2SiCl(CH_2Cl) + CH_3MgBr \longrightarrow (CH_3)_3SiCH_2Cl$

2. $(CH_3)_3SiCH_2Cl + Mg \longrightarrow (CH_3)_3SiCH_2MgCl$

3. $(CH_3)_3SiCH_2MgCl + CF_2=CCl_2 \longrightarrow (CH_3)_3SiCH_2CF=CCl_2$

The first step was carried out by reacting the silane with an excess of methylmagnesium bromide in dibutyl ether and about 120 g of $(CH_3)_3SiCH_2Cl$, b.p. 96-100°, were obtained. The next two steps were carried out by the following procedure. Magnesium (13 g) and dry diethyl ether (250 ml) were added to a flask equipped with stirrer, condenser and dropping funnel and trimethylchloromethylsilane (58 g) added slowly. A few crystals of iodine were needed to initiate the reaction. The excess magnesium was removed by filtration and the solution returned to the flask and 1,1-dichloro-2,2-difluoroethylene (63 g) added and refluxed for six hours and then stored for seven days at room temperature. A previous run carried out for a short time had given none of the desired product. After removal of the solvent, the reaction mixture was distilled at atmospheric pressure to 150° then under reduced pressure until distillation stopped. This product was then redistilled to give 13 g of material, b.p. 104-110° at 95-105 mm, n_D^{23} 1.4222, d_4^{23} 1.1572. Anal. Calcd. for $C_6H_{11}Cl_2FSi$: Cl, 35.3. Found: Cl, 34.5.

C. The Preparation of Phenyltrifluorosilane

$$C_6H_5SiCl_3 + SbF_3 \longrightarrow C_6H_5SiF_3 + SbCl_3$$

Antimony trifluoride (196 g, 1 mole) was added to a flask equipped with a stirrer, dropping funnel and reflux condenser and phenyltrichlorosilane (212 g, 1 mole) was added dropwise. The reaction flask was cooled in ice water. Stirring was continued for 2 hours after the addition and the mixture then allowed to stand for 48 hours. The product was distilled and phenyltrifluorosilane (78 g), b.p. 100-103°, was obtained.

D. The Attempted Reaction of Phenyltrifluorosilane and Bromine

Bromine (80 g) was added dropwise to phenyltrifluorosilane (78 g) in a reaction flask fitted with a condenser connected to cold traps, stirrer and dropping funnel. After addition was completed, the mixture was refluxed for 5 hours. No product was obtained in the cold traps. The bromotrifluorosilane boils at -42° so evidently it was not formed in the reaction.

E. The Polymerization of 3, 3, 3-Trifluoropropylmethyldichlorosilane

Thirty grams of $CF_3CH_2CH_2Si(CH_3)Cl_2$ was added dropwise to 200 g of 10% hydrochloric acid over a period of 15 minutes, stirred for 2 hours and the mixture allowed to stand for 36 hours. The resulting oil was separated and the water layer extracted twice with 25 ml portions of ether. The ether was evaporated and the oily residue added to the original oil. Sixty drops of 5% alcoholic solution of sodium hydroxide were added with stirring over a period of 15 minutes and the mixture heated for 3-1/3 hours to between 120 and 160° and at 200° for 1-1/2 hours. On cooling to room temperature, a viscous liquid was obtained.

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